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Dissociative adsorption of NO upon Al(111): Orientation dependent charge transfer and chemisorption reaction dynamics

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The dissociative and abstractive chemisorption dynamics of NO on Al(111) were studied. A higher sticking probability for the N end-on of NO onto Al(111) was measured. In contrast, Auger electron experiments reveal stepped surfaces to be oxygen rich at low coverage after exposure to NO. Density functional theory calculations show (i) a few angstroms from the surface, an N end-on first collision geometry results in electronic structures consistent with charge transfer; (ii) there is stabilization on the surface for N end-on or side-on orientations; (iii) dissociation is enhanced by a partial or full flip of the molecule. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Simple molecules (e.g., O_2, NO, and Cl_2) and simple metal substrates, like alkalis and aluminum, ought to provide model systems to study molecule–surface interactions. The halogen/alkali case, e.g., Cl_2 on K, forms a unique class of gas-surface reactions with phenomena like exoelectron emission[1] and chemiluminescence[2] that are modeled with nonadiabatic and diabatic events.[3–5] The O_2/Al(111) chemisorption system may also involve nonadiabatic processes. Experimental work and adiabatic theoretical models support the existence of a molecularly adsorbed state and abstractive chemisorption yielding single O-adatoms on the surface and atomic O-atoms in the gas phase.[3,6–8] However, a nonadiabatic model[9] is probably required to explain the activated sticking probability[7] and the observed chemiluminescence.[5,10]

In order to clarify the underlying mechanism of the initial oxidation of aluminum, we have studied the reaction between a heteronuclear diatomic molecule, nitric oxide, and the Al(111) surface. There are four principle results: (1) The average sticking probability (S_0) versus incident energy (E_i) exhibits characteristics of a predominantly activated process. (2) The sticking probability of oriented NO is highest for N end-on collisions. (3) Auger electron spectroscopy shows more oxygen than nitrogen adatoms at low coverage on stepped surfaces. (4) First principles calculations are consistent with a very simplified model in which the NO molecule partially or fully flips during the chemisorption process: (i) Charge is most efficiently transferred to the NO molecule having an N end-on orientation. (ii) The saddle point for dissociation in the N-end on orientation is at an inaccessibly long bond length (>2 Å) and energetically above the vacuum level. (iii) A lower barrier (about 0.4 eV) for dissociation of NO exists when the molecular axis is parallel to the surface (side-on), but the barrier with a saddle point at the smallest bond length (1.7 Å) is for an O end-on orientation. In a simplified picture, NO reacts with Al(111) by a

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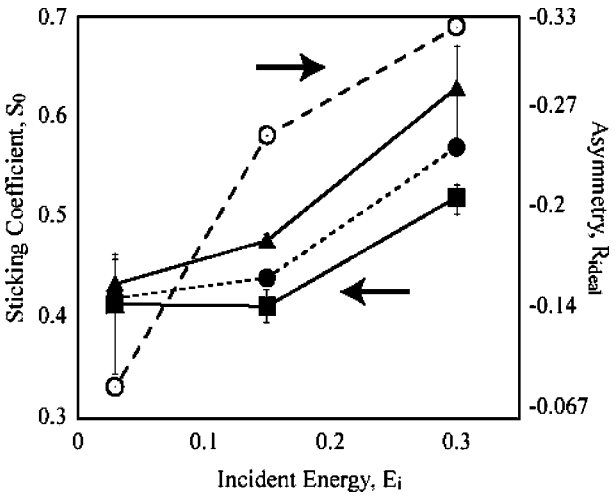

FIG. 1. Oriented NO molecular beam sticking probability on Al(111). Left side: Initial sticking probability of NO as a function of incident energy for N-end (▲) and O-end (■) preferentially oriented molecular beams. Right side: Sticking probability asymmetry (○) as a function of incident energy. Vertical error bars are standard deviations.

N-end first collision that initiates charge transfer, but dissociation of the molecule requires a rotation of the molecule that results in abstractive chemisorption near step edges.

This paper will present the results from the orientation experiment, the Auger experiment, and the density functional theory (DFT) calculations sequentially followed by a discussion. The techniques for each experiment will be described before the corresponding results.

II. ORIENTATION EXPERIMENTS

The orientation experiments were performed to determine the preferred orientation for the initial charge transfer between NO and Al(111). In the oriented molecular beam apparatus,[11] an Al(111) crystal was cleaned by sputter and anneal cycles until no peaks of O and C were observed in Auger measurements. A pulsed valve created NO gas pulses seeded in inert gas in order to vary the incident energy. A hexapole lens was used to focus the upper level of the Λ-doublet $^2\Pi(J=0.5)$ of ground state NO through a 5 mm diameter aperture into a UHV chamber. The NO signal for hexapole on versus off rose by a factor of five. The state selected NO beam was oriented in a homogeneous electric field prior to impact with the surface at 15° incident angle by a stainless steel rod positioned 1 cm in front of the Al(111) crystal with a bias of ± 15 kV. Sticking probability measurements were performed by the reflectance technique[12] using a mass spectrometer.

The initial sticking coefficients of preferentially oriented NO on the Al(111) surface, S_0^{N}, S_0^{O}, and S_0^{ave} are plotted in Fig. 1 (left *y*-axis). The initial sticking coefficients have been corrected for the interaction between NO and the experimental vacuum chamber walls.[13] The mean value of the initial sticking coefficient, $S_0^{\mathrm{ave}}=(S_0^{\mathrm{N}}+S_0^{\mathrm{O}})/2$, agrees reasonably well with measurements carried out with an unoriented beam.[14] S_0^{ave} is enhanced by increasing translational energy. Extrapolating the more extensive sticking data from an unoriented beam to thermal energies (0.025 eV), the sticking probability still does not go to zero.[14] Since some molecular orientations and/or surface impact sites have no barrier to dissociation, we denote the dissociation as ''predominantly'' activated.

The steric asymmetry is the relative difference in sticking probability for the two orientations, $R_{\mathrm{meas}}=2\cdot(S_0^{\mathrm{O}}-S_0^{\mathrm{N}})/(S_0^{\mathrm{O}}+S_0^{\mathrm{N}})$. Previous experiments have ascertained that a correction factor, C, must be applied to R_{meas} to account for nonideal effects: $R_{\mathrm{ideal}}=C\cdot R_{\mathrm{meas}}$, $C=1.7\pm0.18$.[15] The negative value for R_{ideal} (Fig. 1, right *y*-axis) indicates that the preferred molecular orientation is an N end-on collision. This result is consistent with the chemisorption being initiated by charge transfer from the surface into the NO π^* LUMO, which is weighted towards the less electronegative nitrogen atom. A simple calculation of the NO π^* LUMO end-on cross sectional area predicts a steric asymmetry of -0.4; therefore, the measured steric asymmetry for the reaction is consistent with the orbital asymmetry of the molecule. The -0.4 steric asymmetry does not necessarily imply that only N-end first collisions react, instead it implies that N-end first collision are about twice as reactive as other orientations.

Figure 1 indicates that R_{ideal} increases with E_i. At low E_i, the small absolute value of R_{ideal} may be explained by an orientational steering process in which incident molecules are steered by the surface into N end-on collisions. N end-on preferred orientational steering has been modeled to promote reactions between low E_i NO and metal surfaces.[16] At high E_i, molecules scatter from the repulsive wall of the surface before effective reorientation to an N end-on collision can occur. Alternatively, the smaller orientation effect observed at low kinetic energies is consistent with the low energy precursor mediated chemisorption being independent of orientation.

III. CHEMICAL SELECTIVITY EXPERIMENTS

The chemical selectivity experiments were performed to determine if NO undergoes chemically selective abstraction; the chemical selectivity shows the preferred orientation of NO during the breaking of the internal bond. Auger electron spectroscopy (AES) measurements have been used to examine the chemical selectivity of the NO+Al(111) reaction. The Auger experiments were conducted independently at University of California-San Diego and Göteborg on different crystals, in different UHV systems,[17] by different teams to be certain of their veracity. In each experiment, an Al(111) crystal was cleaned by sputter and anneal cycles. The surfaces were checked for cleanliness and order by AES and low energy electron diffraction (LEED). The 300 K surfaces were dosed with NO molecular beam seeded in inert gas. The nitrogen to oxygen ratio (N/O) was obtained from measurements of AES differential peak-to-peak values for N and O, calibrated with appropriate sensitivity factors from the literature.[18] In Fig. 2(a) the AES spectra peaks are also used to measure the absolute coverage (*x*-axis), whereas in Fig. 2(b) the absolute coverage (N+O) is obtained from ''chopped'' sticking probability measurements[12] calibrated as a percentage of saturation.

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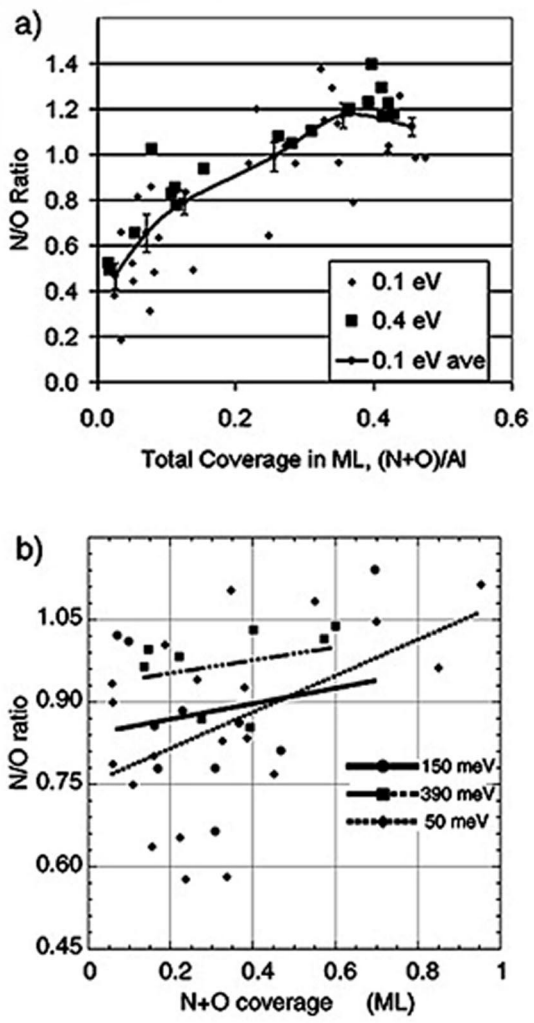

FIG. 2. Absolute O to N atomic adsorbate concentrations of unoriented NO reacting with Al(111). The N/O ratio was calculated from the Auger electrons signals of O-KLL and N-KLL lines with a 1.5 relative sensitivity ratio. (a) La Jolla data from dosing with 110 meV (♦ small) and 400 meV (■) NO. The line and standard error bars are for binned means (○) of the 110 meV data. (b) Göteborg data for N/O ratio with 50 meV (♦), 150 meV (●), and 390 meV (■) NO dosing.

Figure 2(a) (La Jolla) was obtained by dosing an Al(111) crystal that exhibited a loss of optical specularity (matte finish) after it was sputtered and annealed in UHV.[19] In addition, LEED images exhibited satellite peaks built onto the 1×1 pattern indicating a highly stepped (2%–5%) or faceted surface. For the lowest detectable adsorbate coverage ($\sim$0.03 ML), N/O equals 0.5: Oxygen-selective abstractive chemisorption ($NO_{(g)}+Al_{(s)}\rightarrow O\text{-}Al_{(s)}+N_{(g)}$) occurs in the 0–0.2 ML regime. The N/O ratio is stoichiometric, within experimental error, at higher coverage. The chemical selectivity is slightly higher for low translational energy NO. We note that on the clean surface, no oxygen was detected ($<$0.005 ML); therefore the N/O ratio of 0.5 measured at low coverage is not due to contamination.

Figure 2(b) (Göteborg) shows the quantitative ratio of nitrogen to oxygen surface adsorbates versus total adsorbate coverage in a separate experiment. The crystal morphology has been checked with He reflectivity measurements. For a 50 meV NO beam, a N/O ratio of 0.75 is observed at low adsorbate coverage. The N/O ratio again approaches unity as the beam energy or adsorbate coverage increases. Similar trends are obtained from integral spectra analysis of the AES peaks and satellites.

Because there is scatter in the data, a standard error analysis was performed. For 60 measurements with an incident NO translational energy of 0.1 eV, the total adsorbate coverage was binned into 0 to 0.05 ML, 0.05 to 0.1 ML, 0.1 to 0.2 ML, 0.2 to 0.3 ML, 0.3 to 0.4 ML, and 0.4 to 0.5 ML. This analysis is displayed in Fig. 2(a); the mean N/O ratio increases from 0.47 ± 0.056 (standard error) at 0.026 ML coverage to a mean N/O ratio 1.12 ± 0.04 at 0.45 ML coverage.

Three sets of checks were made to insure that the chemical selectivities recorded at low coverage are not due to experimental artifacts. (a) The Auger electron beam could alter the adsorbate coverage on the NO covered surface. The change in the oxygen and nitrogen Auger peaks on a surface with a 1/4 ML of NO was recorded while the surface was exposed to the Auger electron beam (see EPAPS archive Fig. 1).[23] The nitrogen peak was stable, but the oxygen to aluminum ratio increased by 0.0004/min (sensitivity corrected). During a regular experiment, the electron beam is on a single spot for 45 sec so the maximum increase in oxygen/aluminum ratio would be less than 0.0004 which is insignificant. (b) The low coverage measurements are made at the edge of the dose spot; therefore, electron beam induced NO, N, or O chemisorption on the clean surface at the edge of the dose spot might be important. After 15 min of exposure to the electron beam, we found no detectable chemisorption on the clean portions of the sample (see EPAPS archive Fig. 2).[23] Since our detection limit is about $O/Al=0.001$ (sensitivity corrected), the experiment shows that the electron beam induced chemisorption changes the O/Al ratio during a 45 sec experiment by less than 0.001. (c) As a final check, we measured the chemical selectivity at very low coverage on a completely flat surface. This surface had a perfect LEED pattern and STM showed it had very large terraces ($>$300 Å). At both 0.016 and 0.043 ML coverage, the O:N ratio was 0.99 ± 0.10 and 1.13 ± 0.02 (where the errors are standard errors).

These results offer direct experimental evidence that the reaction between NO and the clean Al(111) surface often leads to the formation of only one bound adsorbate on stepped surfaces, $O\text{–}Al_{(s)}$, while the N-atom is ejected back into the gas phase. Since the binding energy of a single O-atom to the Al(111) surface (7.5 eV)[20] is larger than the bond strength of NO (6.2 eV), oxygen selective abstraction is thermodynamically allowed.

IV. DFT CALCULATIONS

The DFT calculations reveal why the molecule rotates during the chemisorption process. The calculations presented are based on DFT;[21] calculations using similar methodologies have been published.[8,22] Total energies in three NO molecular orientations are calculated for different intramolecular distances (d_{N-O}) and different molecule center-of-mass to surface distances (Z) in steps of 0.2 and 0.5 Å, respectively.

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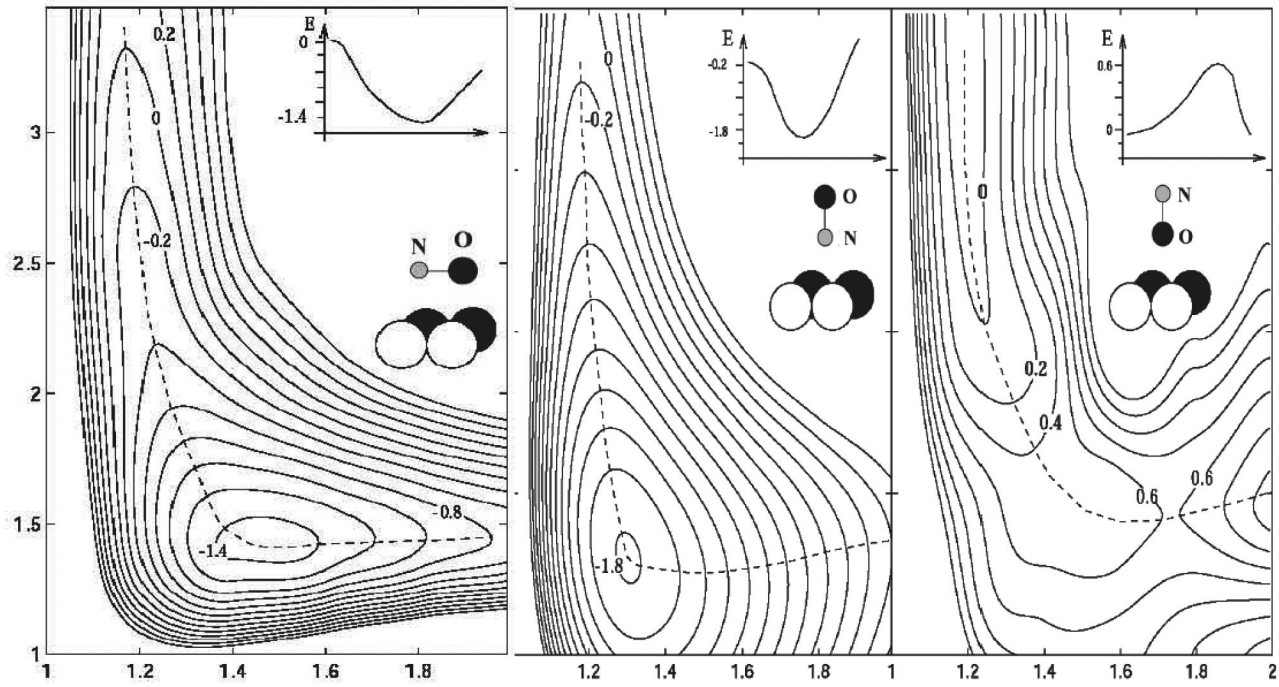

FIG. 3. Cuts through the six-dimensional PES of NO as a function of bond length (d_{N-O}) and distance above the Al(111) surface (z). Cartoon inset depicts the NO molecular orientation for each PES. Inset plots show the potential energy along the reaction path that is indicated by the dashed line on the PES.

The results are compiled to obtain potential energy surfaces describing the adiabatic interaction for each molecular orientation.

The theoretical results presented in Fig. 3 show two-dimensional cuts through the calculated adiabatic potential energy surface (PES) of the NO–Al(111) interaction for three different NO molecular orientations. The results demonstrate that there is a molecular chemisorption well with a depth of 1.4 and 1.8 eV for side-on and N end-on orientations, respectively. The calculated local density of states (LDOS) for the NO molecule in the well for side-on and N end-on orientations is consistent with a local electron configuration like the "NO^{2-}" state.

The calculated occupancy of $2\pi^*$MO-resonance indicates that under adiabatic conditions charge has been transferred to the incident NO molecule even before it reaches the potential well. At a distance of 3.0 Å above the Al surface, the NO minority spin $\pi^*_{x,y}$ molecular orbital (MO), which is empty in the free molecule, is already partially occupied for an N end-on molecule. Conversely, the occupation of the $\pi^*_{x,y}$ MO resonance is negligible in the side-on and O end-on molecular orientations at $Z=3.0$ Å. These calculations indicate that electron transfer to the molecule is most favorable for N end-on collisions which is consistent with our experimental results.

From the molecular chemisorption well, there is an anisotropic barrier to dissociation. The stable molecular well (N end-on) has a depth of 1.8 eV, and the barrier for dissociation from this well is at least 2.4 eV. Even worse, the saddle point for the N end-on barrier occurs for a highly elongated bond (>2 Å) so the molecule cannot efficiently use either the energy liberated from molecular chemisorption energy or thermal energy to surmount the dissociation barrier. The molecular well for a side-on NO is 1.4 eV deep, with a dissociation barrier of at least 0.8 eV again having a highly elongated bond. In contrast, an O end-on NO has no chemisorbed molecular minimum and a dissociation barrier of 0.6 eV above the energy of the free molecule. Furthermore, the barrier for dissociation in an O end-on configuration occurs at only a modestly extended bond length. Since the barrier for O end-on orientation is above the vacuum level, we do expect that some of the molecules will dissociate in a side-on orientation and would only provide chemically selective abstraction near step edges; however, step edges are common on highly stepped surfaces (2%–5%) where we experimentally observe the greatest chemical selectivity in NO/Al(111) chemisorption.

To relax into the bottom of the chemisorption well, the molecule has to descend the vibrational ladders in many steps. The three vibrational modes in order of decreasing energy are the N–O stretch, the NO-metal stretch, and a frustrated rotation. Assuming the vibrational lifetime of each mode is about 5–10 vibrational periods and the frustrated rotation is long-lived, then before the molecule has reached an energy corresponding to the dissociation barrier level of side-on NO, it has undergone many frustrated rotations. Some of these rotations will convert an N end-on NO to a temporary side-on orientation, increasing the probability for dissociation. Figure 3 predicts that the NO center of mass moves upwards upon dissociation of the molecule, which may lead to abstraction.

Our combined experimental and theoretical work shows that that the reaction of NO with aluminum is a two-step process including a change of the orientation of the molecule with respect to the surface. There is a strong attraction between the surface and the N end-on of the molecule. How-

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ever, the energetic barrier and the bond length at the saddle point are reduced along the pathway to dissociation as the molecule changes from N end-on to side-on or even O end-on orientation.

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